D02 QUALITATIVE AND QUANTITATIVE STUDY OF ASPHALTENES PRECIPITATION DURING A GAS INJECTION PROJECT

S. Sfakiotakis[1], N.Pasadakis[1], N.Varotsis[1] and H.P.Hjermstad[2]

[1]*Technical University of Crete, Greece*
[2]*DewPoint AS, Norway*

Abstract

Laboratory and field data from the Snorre reservoir oil in the North Sea confirm that asphaltenes, due to the fact that they precipitate when the oil in which they are contained is subjected to considerable compositional changes, can be used as a natural tracer for monitoring the success of a gas miscible flooding during IOR projects.

The field data reveal that the change of GOR in producing wells affects the asphaltenes content of the producing oil only in the cases where injection gas has gone into solution. A series of single and multiple -both forward and backward- contacts were performed in the laboratory to simulate the compositional changes that the Snorre reservoir oil undergoes during a gas injection project. The asphaltenes solubility during the single contacts was reduced by increasing the amount of dissolved gas in the oil. During the forward contacts, asphaltenes precipitation increased as the number of contacts increased, while during the backward contacts, the opposite trend was observed.

Furthermore, compositional characterisation of the precipitated asphaltenes produced under different experimental conditions provides a better understanding of the precipitation process.

Introduction

It is well known that asphaltenes precipitation occurs when reservoir fluids undergo compositional changes such as when gas is injected into under-saturated oil reservoirs during miscible flooding [1], [2]. Variation in the concentration of asphaltenes measured during reservoir depletion can provide qualitative estimates of the success of a gas miscible flooding while the integration of these data into the reservoir simulation model can pinpoint the areas where the gas has gone into solution or not. This can lead towards a better reservoir management and decision making for achieving higher recovery factors, extension of the production plateau as well as reduction of the unnecessary energy consumption and CO_2 emission from the power stations that produce the energy for the compression of the injected gas.

Numerous field data during the application of enhanced oil recovery in the Snorre field confirm the concept of change in the asphaltenes solubility with the change of the dissolved injected gas amount. One and half year after the field came on production in August 1992, a WAG pilot was started in the central fault block (CFB) of the field with down flank injection of separator gas. The oil was initially strongly undersaturated with 25 MPa difference between reservoir pressure and bubble point pressure. The minimum miscibility pressure is 28 MPa and the reservoir pressure was maintained at around 30 MPa.

An early gas breakthrough was experienced in well P-18, one of the CFB producers, after only one month of gas injection. The well was closed due to gas limitation in the process and the following two years this well was only opened for short periods. Asphaltenes depositions in the tubing were seen in all PLT surveys.

The asphaltenes content in some of the CFB producers has been monitored regularly from summer 1998 in the produced separator oil. Prior to that, only few measurements were available in order to investigate whether the change in asphaltenes content could be related to the amount of increased solution gas content of the produced oil. Tracer injections, PLT surveys, saturation logging (RST) and reservoir simulations have not been able to answer conclusively if the injected gas primarily was dissolved in the oil or moved as a free gas phase.

The extend to which the injection gas exists in the reservoir as a free gas phase is a keypoint in understanding the recovery mechanism at work in the Snorre CFB. The changes in the n-pentane asphaltenes content of one of the CFB producers are given in Figure 1. One can observe a clear decreasing trend with time for the well P-18 after gas breakthrough. The asphaltenes monitoring program was discontinued in May 2002 due to poor accuracy in the measurements. Frequently, asphaltenes values significantly higher than the content of the initial reservoir fluid were reported and the reproducibility of the analysis on parallel samples was poor. It was not possible to establish trends with time or GOR. In April 2002, the collection of separator oil samples for asphaltenes monitoring of the producers restarted as part of the MOREOIL project [3] with an improved analytical method for measurement of the asphaltenes content. The project now concentrated on the western fault block (WFB) where the WAG injection had been started in September 1995.

The asphaltenes content of the produced oil from the WFB producers varies. The oil was depleted differently depending on the producing GOR. There was not the same relationship between the asphaltenes content in the produced oil and the producing GOR in the WFB producers. Gas breakthrough has not occurred in well P-43 and the asphaltenes content of the produced oil is unchanged within the accuracy of the measurements as shown in Figure 2.

On the other side, the asphaltenes content decreases with GOR after gas breakthrough in well P-24, as shown in Figure 3 while before gas breakthrough, the asphaltenes value was the same as seen in well P-43. Other wells (P-33, P-39) from the same fault block give lower asphaltenes content in the oil after gas breakthrough, but the decrease is less than the observed for well P-24. Some asphaltenes precipitation occurs when the pressure decreases from bottomhole to the sampling point in the test separator. Undepleted single-phase bottom hole samples have shown that the asphaltenes content of the reservoir oil is about 1.2 weight-%, whereas the value obtained on the separator oil samples not affected by injection gas is about 0.8 w-% regardless of well. This shows that precipitation due to the pressure change in the tubing is about constant and that the main difference seen between samples has to be related to the compositional effect of injection gas going into solution in the undersaturated reservoir oil.

Different amount of injection gas has gone into solution in wells P-24, P-33 and P-39. All these wells have gas breakthrough and are producing with excess gas. The asphaltenes content is decreasing mostly in P-24 indicating that most of the excess gas produced has been in solution while a significant part of the gas produced in wells P-33 & P-39 has to be moving as a free gas phase in the reservoir.

A laboratory project was initiated in order to investigate some of the key issues occurred. A series of experiments involving phase behaviour and asphaltenes precipitation studies of the Snorre reservoir oil and its mixtures with injection gas were established. Additionally, tuning of

the PVT and precipitation data was carried out using a commercial phase-behaviour package to produce an accurate PVT model to be incorporated to an advanced reservoir simulator.

Method for measuring the asphaltenes content

The method for measuring the asphaltenes content which was used during this study is a modification of the IP 143 separation method [4]. N-pentane as well as n-heptane were used as precipitating agents. The precipitate from the first titration was redissolved in toluene and subsequently precipitated for a second time. Each sample was analysed twice to ensure repeatability. The difference in the yields between the two precipitation steps provides a measure of the amount of waxes or other compounds which remained absorbed in the asphaltenes from the first precipitation. The use of n-heptane as the precipitating fluid yields a product that is different from the n-pentane insoluble material and as expected a larger fraction of n-pentane than n-heptane insolubles in the oil was observed.

In order to establish the method to be followed, 50 samples from the producers in three fault blocks (CFB, WFB and EFB) have been analysed. The measurements of the pentane insolubles gave a better accuracy than the ones of the heptane insolubles. The standard deviation was 2.8 % and 12.1 % for the measurements of the 1st precipitation step using n-pentane and n-heptane respectively, as illustrated in Figure 4. The yields from the 1st and 2nd precipitation stages with n-pentane are given in Figure 5. Any decrease in the n-pentane insolubles below 0.8 % wt, which is the value obtained on the separator oil samples not affected by injection gas, is caused by compositional changes in the reservoir oil from the dissolving injection gas. Finally n-pentane was selected as the precipitating agent due to the higher accuracy of the analyses. The absolute standard deviations for the 1st and 2nd n-pentane precipitation steps measurements were the same (0.017 w-%) The difference in the yields between 1st and 2nd precipitation (25% mean value observed from the experiments) has been assigned to the co-precipitation of high molecular weight waxes or other compounds.

Single contact experiments

In order to investigate the change of asphaltenes solubility when gas is injected into the Snorre reservoir, a series of single contact experiments were performed in the laboratory. Mixtures of recombined reservoir oil from mixed with 35% mol and 50% mol injection gas respectively were tested to measure the dissolved asphaltenes content versus pressure at a range covering both the monophasic and diphasic regions. For each test, a small volume of oil was flashed at ambient conditions, and the n-pentane asphaltenes content was measured on the produced stock tank liquid. The mixture with 35% inj.gas did not exhibit pressure dependence on the asphaltenes precipitation within the accuracy of our measurements as it was also the case for the reservoir oil itself. On the other hand, for the mixture with 50% inj.gas a significant asphaltenes precipitation (0.28% wt precipitated asphaltenes) was observed near the bubble point (28.3 MPa) while the asphaltenes seem to redissolve at lower as well as at higher pressures. This behaviour is in agreement with other published pressure profiles [5] & [6]

Multiple contacts experiments

A series of forward contacts was conducted in the laboratory between the injection gas and the reservoir fluid to simulate the compositional changes that the gas phase undergoes as it advances in the reservoir contacting fresh oil. In addition, a series of backward contacts was also performed to monitor the compositional changes that the less mobile reservoir oil undergoes close to the injection wells as it is repeatedly contacted by fresh injected gas

For the forward contacts, reservoir oil was mixed with injection gas and the mixture was left to equilibrate at 30 MPa and reservoir temperature. Subsequently, the equilibrium gas was brought into contact with fresh reservoir oil for the second forward contact and so on. At each contact, compositional analysis of the equilibrium vapour and liquid phases was carried out. Additionally, a small equilibrium liquid volume was flashed at ambient conditions to measure the n-pentane asphaltenes content of the produced stock tank liquid. The asphaltenes content of the equilibrium liquid decreased as the number of contacts increased (Figure 6)

For the backward contacts, reservoir oil was mixed with injection gas and the mixture was left to equilibrate at 30 MPa and at reservoir temperature. Subsequently, the equilibrium liquid was brought into contact with fresh injection gas for the second backward contact and so on. Compositional analysis of the equilibrium phases and the asphaltenes content measurements were also carried out. In this series of experiments, the asphaltenes seem to redissolve after successive contacts (Figure 6).

Characterisation of the precipitated asphaltenes

Gel Permeation Chromatography (GPC) was employed to reveal possible compositional differences of the asphaltenes produced under different experimental conditions and or different precipitation procedures. Briefly, the analytical set-up consisted of an HPLC pump, two columns 300x7.5 mm with particle size 5μm and 10 μm kept at 40oC and Ultraviolet Diode Array (UV-DAD) and Evaporative Light Scatterring (ELS) detectors. Tetrahydrofuran (THF) at a flow rate of 1ml/min was used as the mobile phase and the sample concentration was 0.1% w/w. The UV-DA detector was utilised because of its sensitivity to the chromophore groups such as the aromatic structures and to the heterocompounds, which constitute the major part of the asphaltenes fraction, while the ELS detector is a mass sensitive device providing a true mass elution profile of the effluent.

Two asphaltenes samples obtained from the STO were produced from the first and the second precipitation step. Their GPC traces from the ELS and UV detectors are presented in Figures 7a, 7b. The inspection of the signals reveals a strong similarity between these two samples particularly for the UV one. The minor difference in the ELS signals can be attributed to the presence of components (in the elution region of C35) in the asphaltenes produced from the single step which are absent in the second one. These components should be considered as saturates, since they are not seen by the UV detector. Additionally, the examination of the average spectra of the two asphaltenes samples from the region of 270-400nm showed also a strong similarity, with their correlation coefficient being higher than 0.999. Therefore, it can be concluded that no discrimination between the chromophore groups present in the asphaltenes samples which were produced from the single and double step procedures was observed.

The signals acquired for the asphaltenes samples precipitated with n-pentane and n-heptane revealed that the n-heptane precipitation method (IP143 method) produces asphaltenes enriched in heavier components. This observation is in agreement with Ancheyta et. al, who reported that the asphaltenes composition is strongly influenced by the precipitation procedure [7]. The ELS signal also showed a significant amount of components eluting as a second distinct peak in the light end of the chromatogram. These components should be considered as saturates (waxes), as they are not seen by the UV detector and according to the experimentally determined elution times they seem to belong in the C20-C30 elution region.

The derived ELS and UV-DAD signals for the asphaltenes produced at the different steps of the forward contacts are presented in Figures 8a, 8b. From the visual inspection of the chromatograms from both detectors, it can be seen that the dissolved asphaltenes in these oils

practically have identical molecular weight distribution, despite the fact that they are present in different concentrations in the oils.

The only noticeable difference between the GPC signals in Figure 8a is the second peak (14min-15min) observed in the ELS chromatograms of the asphaltenes produced from the 1st and 2nd forward contacts, while it is absent in the asphaltenes produced from the 3rd contact. Since this peak can not be detected in the UV chromatograms, it can be attributed to saturated components (waxes) that co-precipitate with the asphaltenes during the third contact experiment.

The examination of the ELS and UV signals of the asphaltenes derived from the backward multiple contacts leads to similar conclusions as the ones derived from the respective forward contacts. From the detectors signals it can be concluded that the asphaltenes of the third backward contact exhibit a slightly heavier molecular weight distribution. From the ELS trace, it is evident that, as it was the case with the samples from the forward contacts, a second peak in the region of lighter components is also present. This peak is absent in the sample of the 3rd contact. Therefore it can be concluded that the waxes co-precipitate in the cell during the third contact experiment.

Conclusions

In this work, field data from the Snorre reservoir oil are presented showing that the change of solution GOR in producing wells affects the asphaltenes content of produced oil and more specifically an increase of GOR leads to a decreasing asphaltenes content. Additionally, a series of single and multiple contact experiments performed in the laboratory confirmed the decreasing trend of asphaltenes content with increasing amount of injection gas. The aforementioned laboratory and field data were integrated into an advanced reservoir simulator, which includes an asphaltenes precipitation model.

A qualitative analysis of the asphaltenes content with Gel Permeation Chromatography coupled with Evaporative Light Scattering, UV-DAD detectors showed that the asphaltenes recovered from samples with different amount of dissolved gas exhibit strong compositional similarity. Some differences on the amount of saturates associated with the dissolved asphaltenes were observed for very high dissolved gas concentrations.

Acknowledgments

References

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[6]   Hirschberg A., de Jong N.J., Schipper B.A., Meyers J.G. : SPE 11202

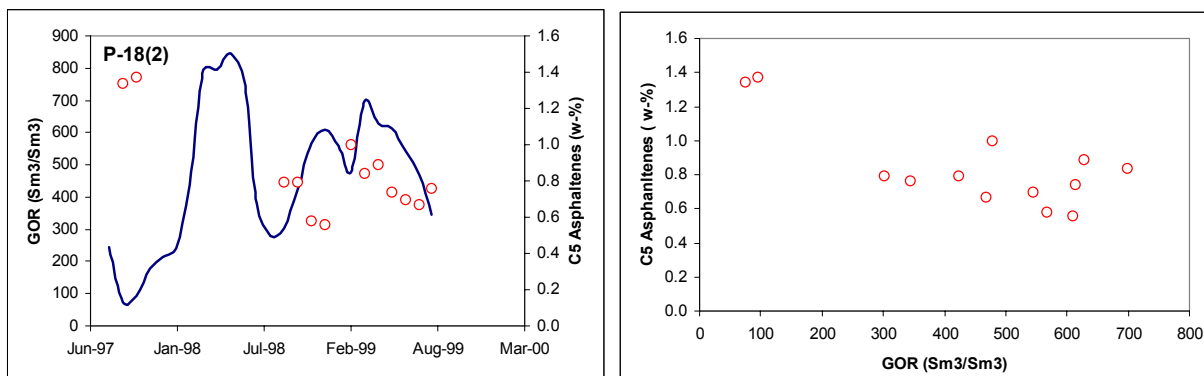[7]   Ancheyta J. et al. : Energy & Fuels. 2002, 16, pp.1121-1127

Figures

Figure 1 Producing GOR in the CFB producer P-18(2) and the asphaltenes content of the stabilised separator oil
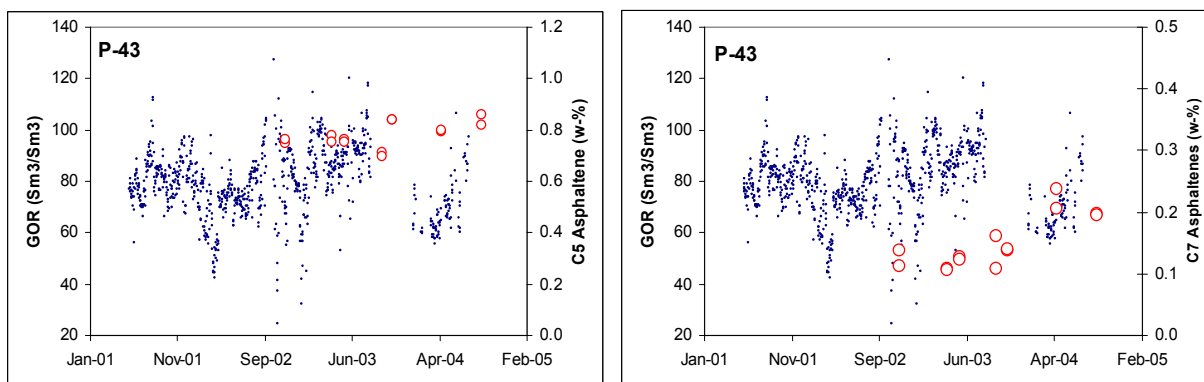

Figure 2 Producing GOR and the asphaltenes content in the WFB producer P-43 before gas breakthrough
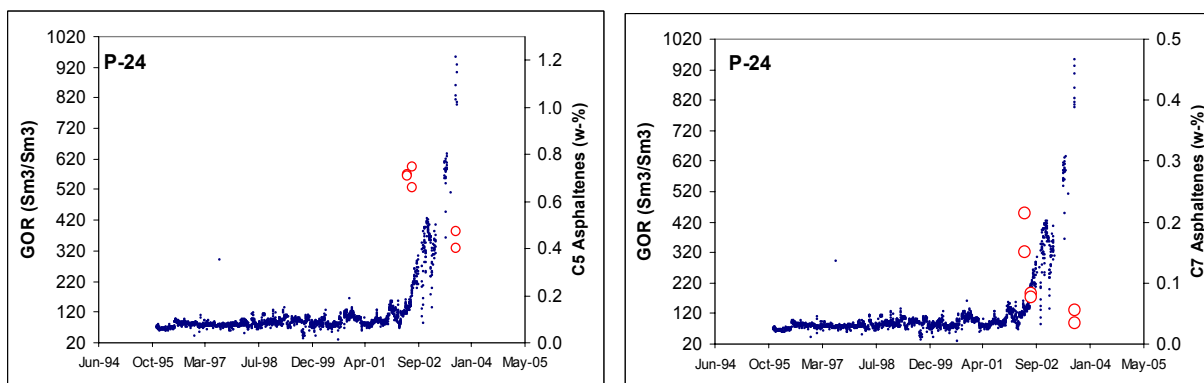

Figure 3 Producing GOR and the asphaltenes content in the WFB producer P-24
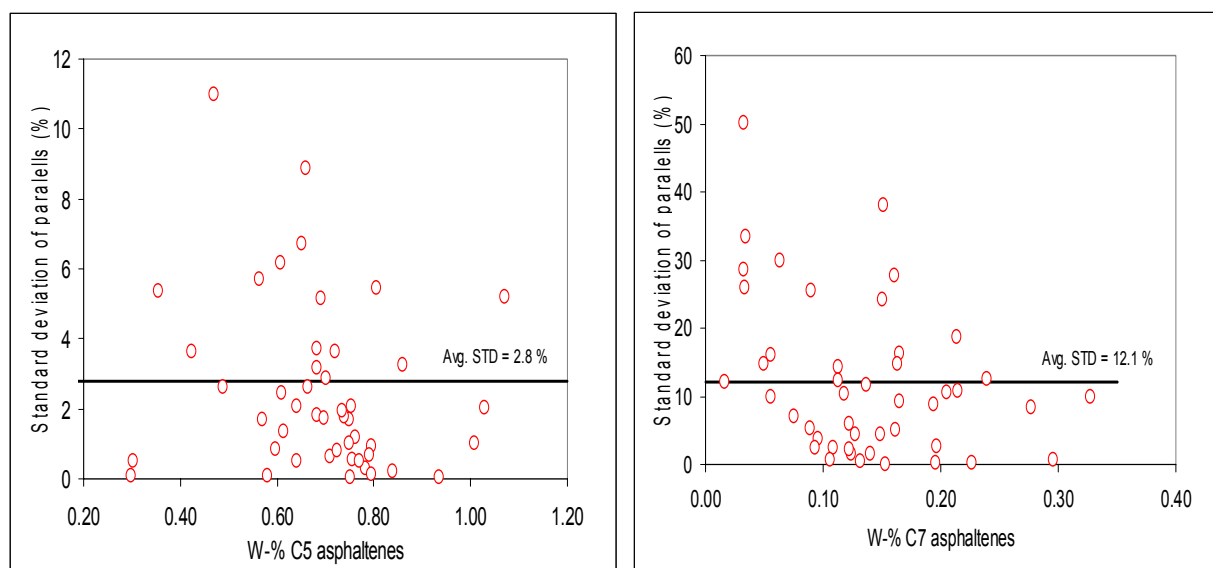
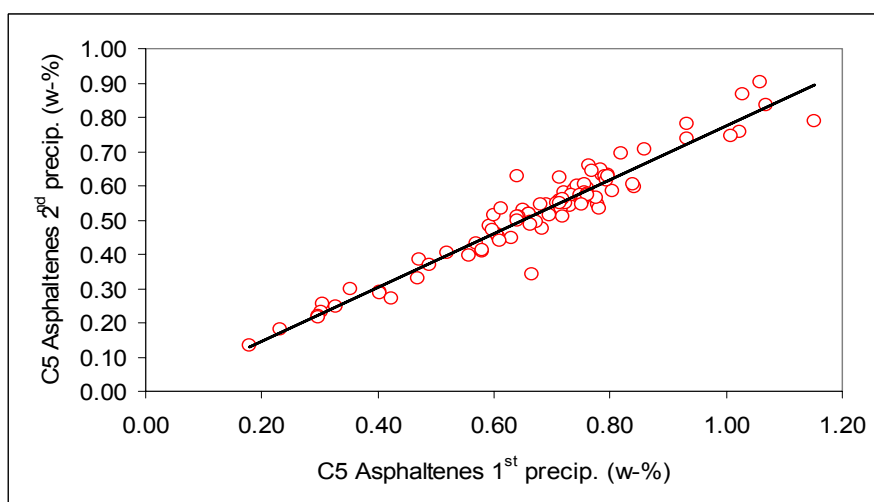**Figure 4** Relative standard deviation beween paralells of pentane and heptane insolubles by 1st precipitation

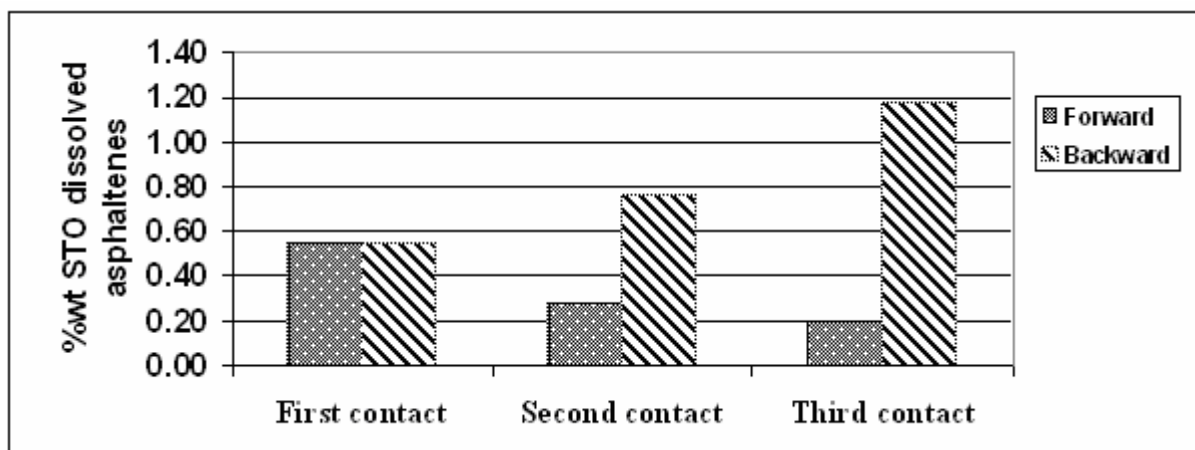**Figure 5** Correlation of pentane insolubles by 1st and 2nd precipitation

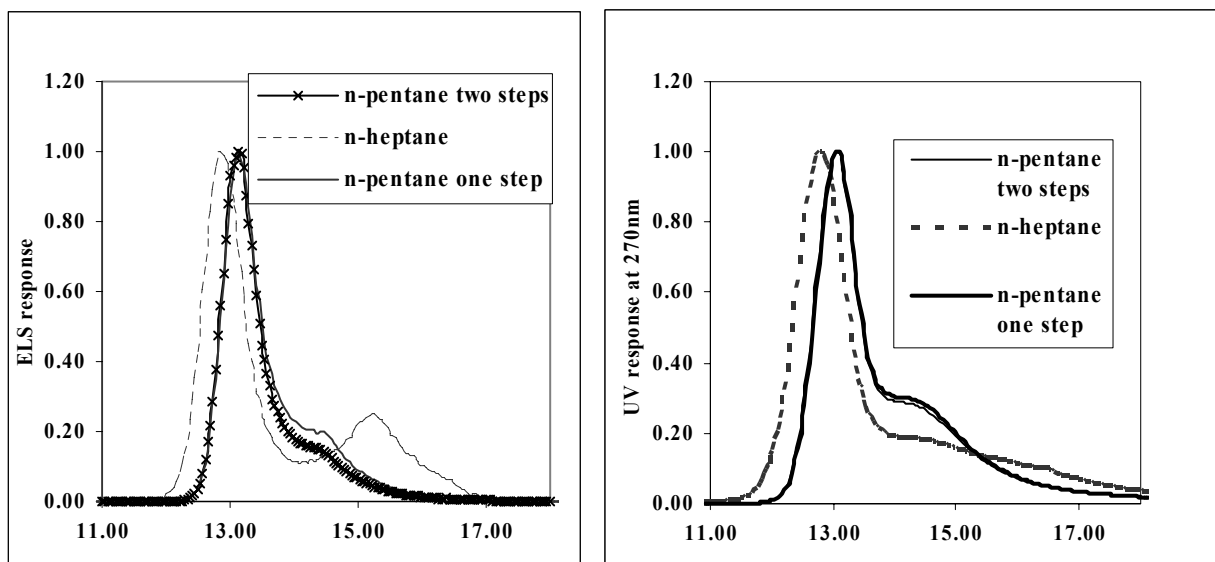**Figure 6**: Change of the asphaltenes content during the multiple contacts

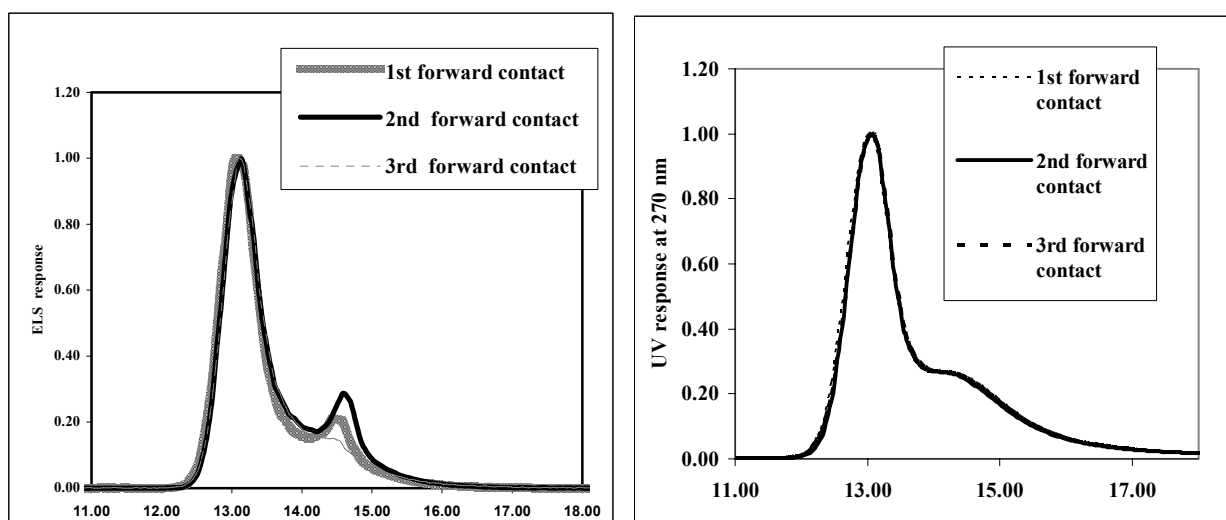**Figure 7a,b**: GPC analysis of the asphaltenes produced with different procedures

Figure 8a,b: GPC analysis of the asphaltenes produced under different experimental conditions